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Quantum Mechanics of a Molecular System Adsorbed on a Dielectric Surface

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Abstract

A molecular system adsorbed on a dielectric surface is modeled as a damped harmonic oscillator driven by a sinusoidal external force. The exact propagator and wavefunction through the Feynman path integral method are obtained. The second-quantization of this system is carried out. Expectation values of several physical quantities are evaluated. The amplitude for transitions between harmonic oscillator states and damped driven oscillator states are obtained explicitly, and the result is applied to a two-level system.

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1. Introduction

The study of time-dependent oscillator systems has received a great deal of attention both in classical and quantum mechanical studies. In the usual quantum-mechanical treatment of these systems, a time-independent Hamiltonian is assumed, which must be obtained through the Legendre transformation of the Lagrangian function which describes the equation of motion for the system.[1] In this context, it is unlikely that all physical oscillator systems have conserved Hamiltonians. The Hamiltonian of a damped driven harmonic oscillator is a typical one with explicit time-dependence. Even though there have been extensive works[2] on this system, this apparently simple system has not been exactly solved quantum mechanically, in contrast to the classical case. Furthermore, the physical interpretations of the Hamiltonian itself and of the time-dependent Schrödinger equation obtained by replacing the canonical momentum with $\frac{\hbar}{i}\frac{\partial}{\partial x}$ in the Kaldirola-Kanai-type Hamiltonian[3] differ among researchers. Some[4] claim that this Hamiltonian (accordingly the Schrödinger equation) describes a dissipative quantum system, while others[5] object to such an interpretation. From the viewpoint of group theory, Cervero et al[6] interpreted it to represent a variable frequency oscillator with minimum uncertainty.

The Feynman path integral formalism[7] provides a general approach to quantum systems. Montroll[8] transformed the original Feynman path integral into a Gaussian integral, and his method was applied by Cheng[9] to evaluate the propagator for a forced harmonic system. Once the propagator suitable to a given system is obtained, the wavefunction of the system is easily calculated. However, even if the Schrödinger equation is solved through the path integral or some other method, there remains the problem of second-quantization. In general, the Hamiltonian for the damped driven harmonic

oscillator (DDHO) is not conserved and not identical to the total energy of the system, giving rise to much difficutly for developing a second-quantization formalism. However, second-quantization, if possible, is important in connection with the problem of finding invariants of a non-conserved system, and for obtaining the coherent states[10] of DDHO.

On the other hand, the optical properties of molecules are greatly altered when they are adsorbed on or near a solid surface. During the past decade, many theoretical and experimental methods have been developed to investigate surface spectroscopy, surface-enhanced Ramann scattering (SERS),[11] resonance fluorescence,[12] photodissociation,[13] etc. There exist, however, several criticisms and controversies regarding the electromagnetic theory.[14] In order to better understand the surface phenomena mentioned above, one must study at the quantum mechanical level the dynamical behavior and optical response of the molecules adsorbed on a solid (metal or dielectric) surface.

In this work, we present a study of the quantum mechanical properties of a molecule adsorbed on or near a dielectric plane surface. We represent the molecule as a polarizable point particle subject to a time-dependent external electric field. We do not consider the nuclear vibrations in this work. In Sec. 2 the classical equation of motion of the induced molecular dipole is given, and this equation is transformed into that of a damped harmonic oscillator driven by an external force. In Sec. 3 the propagator and wavefunction are obtained through the Feynman path integral method. Energy expectation values and dipole moment matrix elements are expressed in Sec. 4. Sec. 5 is devoted to second quantization and calculation of the transition probability between the harmonic oscillator states and damped driven harmonic oscillator states. In Sec. 6 we discuss the results.

2. Classical Equation of Motion for the Dipole Moment

We consider a molecule adsorbed on a dielectric plane surface with complex dielectric constant ϵ and light beam incident from the vacuum side at an angle θ with respect to the z-axis normal to the surface (xy-plane). The normal modes of the incident field satisfy Maxwell's equations subject to appropriate boundary conditions. The wave vector $\vec{k}$ of the field, which is assumed to be independent of frequency, is decomposed into a two-dimensional component $\vec{k}_{\parallel}$ parallel to the surface and a z-component perpendicular to the surface. The electric field vector is polarized in two ways. The first is the s-polarized wave (s-wave) perpendicular to the incident plane defined by $\vec{k}$ and $\vec{z}$ (a vector along the z-direction). The second is the p-polarized wave (p-wave) in the incident plane. The local field $\vec{E}_{\ell}(\vec{r}_m,t)$ at the adsorbed molecule position $\vec{r}_m$ is expressed as

$$\vec{E}_{\ell}(\vec{r}_m,t) = \vec{E}_p(\vec{r}_m,t) + \vec{E}_s(\vec{r}_m,t) \quad . \tag{2-1}$$

where t indicates time. $\vec{E}_p(\vec{r}_m,t)$ represents the primary field, which consists of the field incident directly on the molecule and the field reflected from the solid surface when the molecule is absent, and $\vec{E}_p$ is calculated using the Fresnel formula.[15] $\vec{E}_s(\vec{r}_m,t)$ is the secondary field which represents the field emitted by the induced molecular dipole and reflected back to it from the surface. The induced dipole moment $\vec{\mu}(t)$ is the sum of dipole moments induced by the primary and secondary fields. The classical equation of motion for $\vec{\mu}(t)$ is given by

$$\ddot{\vec{\mu}} + \gamma\dot{\vec{\mu}} + \omega_0^2\vec{\mu} = \omega_0^2\overleftrightarrow{\alpha}\cdot\vec{E}_{\ell} \quad . \tag{2-2}$$

The dots indicate time derivatives, ω_0 is the oscillation frequency of the dipole charge, γ_0 is a natural damping constant which measures the linewidth in the optical processes, and $\overleftrightarrow{\alpha}$ represent the effective molecular polarizability tensor of second rank. In Eq. (2-2) we neglected the magnetic effects on the dipole motion, and hereafter we set the permeability of the surface dielectric to be unity. At the molecular position (0,0,d) the primary field vector is calculated using the Fresnel formulas as

$$E_p(d,t) = E_0 \exp\left[-i(kd\cos\theta + \omega' t)\right] \quad , \tag{2-3}$$

where the components of E_0 are given as

$$\begin{aligned} E_{0x} &= E_0\left\{1 - f_1(\epsilon(\omega'),\theta)\right\}\cos\theta \\ E_{0y} &= E_0\left\{1 + f_2(\epsilon(\omega'),\theta)\right\} \\ E_{0z} &= E_o\left\{1 + f_1(\epsilon(\omega'),\theta)\right\}\sin\theta \end{aligned} \tag{2-4}$$

$$f_1(\epsilon(\omega'),\theta) = \frac{\epsilon(\omega') - [\epsilon(\omega') - \sin^2\theta]^{1/2}}{\epsilon(\omega') + [\epsilon(\omega') - \sin^2\theta]^{1/2}} \exp(2ikd\cos\theta)$$

$$f_2(\epsilon(\omega'),\theta) = \frac{\cos\theta - [\epsilon(\omega') - \sin^2\theta]^{1/2}}{\cos\theta + [\epsilon(\omega') - \sin^2\theta]^{1/2}} \exp(2ikd\cos\theta) \tag{2-5}$$

$$\epsilon(\omega') = \epsilon_1(\omega') + i\epsilon_2(\omega') \quad . \tag{2-6}$$

Here $k = |\vec{k}|$ is the magnitude of the wavevector, and ω' is the angular frequency of the incident field.

The secondary field at the molecule position is expressed as a function of the induced dipole moment,[16]

$$\vec{E}_s(d,t) = \int_{-\infty}^{t} dt' \; \overleftrightarrow{G}_s[d;d;t-t'] \cdot \frac{d\vec{\mu}(t')}{dt'} \quad , \tag{2-7}$$

where $\overleftrightarrow{G}_s$ is the scattering part of the dyadic Green's function.[17,18] Equation (2-7) represents the self-polarization effect of the induced dipole. The electric field emitted by the dipole at an earlier time t' interacts with the surface atom (or molecule), causing it to emit lights by polarization. This emitted field by the surface atom (molecule) interacts with the adsorbed molecule at a later time $t > t'$, adding an extra induced dipole moment, which emits radiation that polarizes the surface atom (molecule) again, etc. Through these self-polarization processes, the secondary field yields a change in the linewidth and oscillation frequency of the dipole. Efrima et al[18] used a Fourier transformation method to solve Eq. (2-7), which gives an integro-differential equation, and applied it to the Raman scattering problem of an adsorbed molecular system. The Fourier transform of the dyadic Green's function $\overleftrightarrow{G}_s(d;d;\omega')$ can be calculated only numerically, since it is given in complicate integral form. To avoid such complexity, we incorporate the effects of the secondary field into the linewidth and the oscillation frequency of the dipole moment. In this manner, we obtain a modified classical equation of motion for the dipole moment,

$$\ddot{\vec{\mu}} + \gamma\dot{\vec{\mu}} + \omega_m^2\vec{\mu} = \omega_0^2\overleftrightarrow{\alpha}(\omega')\cdot\vec{E}_p(d,t) \quad . \tag{2-8}$$

As mentioned above, the self-polarization effects are absorbed within the modified damping constant γ and modified frequency ω_m, whose explicit forms are[19]

$$\gamma = \gamma_0 + \gamma_s$$

$$\omega_m^2 = (\omega_0 + \Delta\omega_m)^2$$

$$\gamma_s = \frac{\omega_0^2}{\omega}\,\hat{n}\cdot\left\{\overleftrightarrow{\alpha}(\omega')\cdot[\mathrm{Im}\ \overleftrightarrow{G}_s(d;d;\omega')\cdot\hat{n}]\right\} \tag{2-9}$$

$$\Delta\omega_m = \omega_0\left[1 - \hat{n}\cdot\left\{\overleftrightarrow{\alpha}(\omega')\cdot[\mathrm{Re}\ \overleftrightarrow{G}_s(d;d;,\omega')\cdot\hat{n}\right\}\right]^{\frac{1}{2}} - \omega_0,$$

where $\overleftrightarrow{G}(d;d;\omega')$ is the Fourier transform of $\overleftrightarrow{G}_s(d;d;t-t')$ and $\hat{n} = \vec{\mu}/|\vec{\mu}|$.

Let us now introduce a coordinate system in which the effective polarizability tensor $\overleftrightarrow{\alpha}$ is diagonal,

$$\overleftrightarrow{\alpha}(\omega') = \alpha_x(\omega')\ \hat{x}\hat{x} + \alpha_y(\omega')\hat{y}\hat{y} + \alpha_z(\omega')\hat{z}\hat{z} \quad , \tag{2-10}$$

where $\hat{x}$, $\hat{y}$ and $\hat{z}$ are unit vectors along the coordinate axes. We assume that the molecule is isotropic and its dipole moment is directed toward the positive z-direction. In this case we can set $\hat{n} = \hat{z}$, and thus only the z-component of the primary field, which is given by Eq. (2-3) through (2-6), is required in the equation of motion. Other molecular dipole moment configurations are similar to this case, so that our method does not lose generality. By this manner, Eq. (2-8) can be rewritten as

$$\ddot{\mu} + \gamma\dot{\mu} + \omega_m^2\mu = f_3(\epsilon(\omega'),\theta)\ e^{-i\omega' t} \quad , \tag{2-11}$$

where

$$f_3(\epsilon(\omega'),\theta) = E_0\alpha(\omega')\omega_0^2\sin\theta\left\{1 + f_1(\epsilon(\omega'),\theta)\right\}e^{-ikd\ \cos\theta} \quad . \tag{2-12}$$

Equation (2-11) can be written in a more familiar form if we take just the real part of the external driving force. After some calculations, we obtain the classical equation of motion for the dipole moment of the adsorbed molecule as

$$\ddot{x} + \gamma\dot{x} + \omega_m^2 x = f(t)/m_0 \quad . \tag{2-13}$$

Here $Qx = \mu$, where Q is the average dipole charge, and m_0 is the mass of the molecule. The form of equation of motion (2-13) is the same as that of the usual damped driven harmonic oscillator, so that f is given as

$$f(t) = g(\omega',\theta)\ \cos(\omega' t - \phi_0) \quad , \tag{2-14-a}$$

$$g(\omega',\theta) = \frac{2E_0 m_0 \omega_0^2\ \sigma(\omega')\ \sin\theta}{Q\ g_3(\omega',\theta)} \left\{g_1^2(\omega',\theta) + g_2^2(\omega',\theta)\right\}^{\frac{1}{2}}$$

$$g_1(\omega',\theta) = \cos\theta\ \cos(kd\cos\theta)\left[\left|\epsilon(\omega')\right|^2\ \cos\theta + R(\omega',\theta)\left\{\epsilon_1(\omega')\cos\eta + \epsilon_2(\omega')\sin\eta\right\}\right] + R(\omega',\theta)\ \cos\theta\ \sin(kd\cos\theta)\left\{\epsilon_1(\omega')\sin\eta - \epsilon_2(\omega')\cos\eta\right\}$$

$$g_2(\omega',\theta) = R(\omega',\theta)\ \cos\theta\ \cos(kd\cos\theta)\left\{\epsilon_2(\omega')\cos\eta - \epsilon_1(\omega')\sin\eta\right\}$$

$$- R(\omega',\theta)\ \sin(kd\cos\theta)\left[R(\omega_1'\theta) + \cos\theta\left\{\epsilon_1(\omega')\cos\eta + \epsilon_2(\omega')\sin\eta\right\}\right]$$

$$g_3(\omega'\theta) = R^2(\omega',\theta) + |\epsilon(\omega')|^2\cos^2\theta + 2R(\omega',\theta)\cos\theta\left\{\epsilon_1(\omega')\cos\eta + \epsilon_2(\omega')\sin\eta\right\} \qquad (2\text{-}14\text{-}b)$$

$$\phi_0 = \tan^{-1}\left\{g_2[\epsilon(\omega'),\theta)/g_1(\epsilon(\omega'),\theta)\right\}$$

$$\eta = \frac{1}{2}\tan^{-1}\left\{\epsilon_2(\omega')/[\epsilon_1(\omega') - \sin^2\theta]\right\} \qquad (2\text{-}14\text{-}c)$$

$$R(\omega',\theta) = \left\{[\epsilon_1(\omega') - \sin^2\theta]^2 + \epsilon_2(\omega')\right\}^{\frac{1}{2}} .$$

To avoid the complicated procedure of evaluating the wavefunction and other quantities involved, we have taken the real part of the driving force. The classical Lagrangian and Hamiltonian function corresponding to the equation of motion (2-13) are given, respectively, as

$$L(\dot{x},x,t) = \left[\frac{1}{2}m_0\dot{x}^2 - \frac{1}{2}m_0\omega_m^2x^2 + f(t)x\right]\exp[\gamma t] \qquad (2\text{-}15)$$

$$H(x,p,t) = \left[\frac{p^2}{2m_0}e^{-2\gamma t} + \frac{1}{2}m_0\omega_m^2x^2 - f(t)x\right]\exp(\gamma t) \quad , \qquad (2\text{-}16)$$

where p is the canonical momentum.

3. Propagator and Wavefunction

Recently Um et al[20] have treated a quantum damped driven harmonic oscillator with the path integral method.[7] Following their formalism, we solve the Schrödinger wave equation

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\psi(x,t) \quad , \tag{3-1}$$

where the Hamiltonian operator $\hat{H}$ is obtained by making the replacement $p \rightarrow -i\hbar \frac{\partial}{\partial x}$ in Eq. (2-16). Adopting a Gaussian form for the propagator K,

$$K[x(t),t;x(0),0] = A_0 \exp\left[-a(t)x^2 e^{\gamma t} - b(t)x e^{\gamma t/2} - c(t)\right] \quad , \tag{3-2}$$

which satisfies the wave equation

$$i\hbar \frac{\partial K}{\partial t} = \hat{H}K \quad , \tag{3-3}$$

we obtain three first-order differential equations for the coefficents in the propagator. These differential equations are readily solved by the boundary condition that K reduces to the propagator for a damped harmonic ocsillator[21] when there is no driving force. Through the above procedure we obtain an explicit form for K,

$$K[x(t),t;x_0,0] = \left[\frac{m_0 \omega e^{\gamma t/2}}{2\pi i \sin(\omega t)}\right]^{1/2} \exp\left[A_1(t)x^2 - A_2(t)x\right]$$

$$\times \exp\left[-A_3(t)x_0^2 + A_4(t)x_0\right] \quad , \tag{3-4}$$

where $x_0 = x(0)$ and $\omega = (\omega_m^2 - \gamma^2/4)^{1/2}$ represents the reduced frequency, which will be assumed to be real throughout the present text. The coefficients in Eq. (3-4) are given as

$$A(\omega', \theta) = g(\omega', \theta)/b_1(\omega')$$

$$b_1(\omega') = \left[(\gamma\omega')^2 + \left\{\omega^2 - \omega'^2 + \gamma^2/4\right\}^2\right]^{1/2}$$

$$\phi_1 = \tan^{-1}\left[\gamma\omega'/(\omega^2 - \omega'^2 + \gamma^2/4)\right]$$

$$A_1(\cdot) = \frac{m_0\omega}{2i\hbar} e^{\gamma t}\left\{\frac{\gamma}{2\omega} - \cot(\omega t)\right\}$$

$$A_2(t) = \frac{A(\omega', \theta)\omega}{i\hbar} e^{\gamma t}\left[\left\{\frac{\gamma}{2\omega} - \cot(\omega t)\right\}\cos(\omega' t - \phi_0 - \phi_1) - \frac{\omega'}{\omega}\sin(\omega' t - \phi_0 - \phi_1)\right] \tag{3-5}$$

$$A_3(t) = \frac{m_0\omega}{2i\hbar}\left\{\frac{\gamma}{2\omega} + \cot(\omega t)\right\}$$

$$A_4(t) = -\frac{A(\omega', \theta)\omega}{i\hbar \sin(\omega t)} e^{\gamma t/2}\cos(\omega' t - \phi_0 - \phi_1) + \frac{m_0\omega x}{i\hbar \sin(\omega t)} e^{\gamma t/2}$$

The wavefunction, $\psi_n(x,t)$, of the dipole moment at time t is obtained by the formula

$$\psi_n(x,t) = \int_{-\infty}^{\infty} dx_0\, K[x,t;\, x_0,0]\, \psi_n(x_0,0) \quad , \tag{3-6}$$

where $\psi_n(x_0,0)$ is the wavefunction of a damped harmonic oscillator with the reduced frequency ω. Combining Eqs. (3-4) and (3-6), we obtain

$$\psi_n(x,t) = \left[\frac{D(t)}{2^n n!\sqrt{\pi}}\right]^{\frac{1}{2}} \exp\left[-i\left(n+\frac{1}{2}\right)\cot^{-1}(\xi(t))-B_3(t)\right] \exp\left[-B_1(t)x^2+B_2(t)x\right]$$

$$\times H_n[D(t)(x-E(t))] \quad , \tag{3-7}$$

where

$$\xi(t) = \frac{\gamma}{2\omega} + \cot(\omega t)$$

$$D(t) = \left[\frac{m_0\omega e^{\gamma t}}{\hbar\, \zeta_1(t)}\right]^{\frac{1}{2}}$$

$$E(t) = \frac{A(\omega', \theta)}{m_0} \cos(\omega' t-\phi_0-\phi_1)$$

$$B_1(t) = \frac{1}{2} D^2(t) \left[1 + i\zeta_2(t)\right]$$

$$B_2(t) = D^2(t)\, E(t) \left[1 + i\zeta_3(t)\right] \tag{3-8}$$

$$B_3(t) = \frac{1}{2} D^2(t)\, E^2(t) \left[1 + i\xi(t)\right]$$

$$\zeta_1(t) = \sin^2(\omega t) \left[1 + \xi^2(t)\right]$$

$$\zeta_2(t) = \xi(t) + \zeta_1(t) \left[\frac{\gamma}{\omega} - \xi(t)\right]$$

$$\zeta_3(t) = \zeta_2(t) - \zeta_1(t) \frac{\omega'}{\omega} \tan(\omega' t-\phi_0-\phi_1) \quad .$$

From now on, we shall use the notation $\xi(t) = \xi$, $\xi_1(t) = \xi_1 \ldots$ $D(t) = D$, etc. for simiplicity whenever there is no ambiguity. In obtaining the wavefunction we have used the identity

$$\exp\left[\pm in \cot^{-1} y\right] = \left[1 + y^2\right]^{-\frac{n}{2}} [y \pm i]^n \quad . \tag{3-9}$$

We find the following useful relations between the coefficients in the exponential terms of the wavefunction,

$$B_1 + B_1^* = D^2, \quad B_2 + B_2^* = 2D^2E, \quad B_3 + B_3^* = D^2E^2 \quad , \tag{3-10}$$

which are used in later calculations.

4. Energy Expectation Values and Matrix Elements of the Dipole Moment

Using the Lagrangian of Eq. (2-15), the mechanical energy operator of the system is easily obtained as

$$E_{op} = -\frac{\hbar^2}{2m_0} e^{-2\gamma t} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m_0 \omega_m^2 x^2 - xf(t) \quad . \tag{4-1}$$

We note that above energy operator is not identical to the Hamiltonian $\hat{H}$ itself. $\hat{H}$ does not represent the total energy of the system, but rather is the generator of the motion of an energy-dissipative open system.[22] Equation (4-1) is the same as Eq. (6-1) in Ref. 20 except for the xf(t) term. It is straightforward to calculate the matrix elements of the energy operator:

$$\langle E_{op}\rangle_{m,n} = \frac{m_0\omega_m^2}{2D^2}\left[\sqrt{(n+1)(n+2)}\ (\tfrac{1}{2} - 2\lambda_1 B_1)\delta_{m,n+2} + \sqrt{2(n+1)}\right.$$

$$\times\ (DE + 2\lambda_1\lambda_2 B_1 - D\lambda_3)\delta_{m,n+1} + \left\{(n+\tfrac{1}{2}) + 2(2n+1)\lambda_1\lambda_4 B_1 + D^2E^2 - \lambda_1\lambda_2^2 - 2D^2E\lambda_3\right\}\delta$$

$$\left. + \sqrt{2n}\ (DE - 2\lambda_1\lambda_2\lambda_4 - D\lambda_3)\delta_{m,n-1} + \sqrt{n(n-1)}(\tfrac{1}{2} - 2\lambda_1\lambda_4^2 D^2)\delta_{m,n-2}\right]$$

$$\times\ \exp\left[i(m-n)\ \cot^{-1}(\xi(t))\right]\quad , \qquad (4\text{-}2)$$

where

$$\lambda_1(t) = \left[\frac{\omega}{\omega_m \zeta_1 D^2}\right]^2\quad ,\ \lambda_2(t) = D[B_2 - 2B_1 E]$$

$$\lambda_3(t) = \frac{A(\omega',\theta)b_1(\omega')}{m_0\omega_m^2}\cos(\omega' t - \phi_0)\quad ,\ \lambda_4(t) = D^2 - B_1\quad . \qquad (4\text{-}3)$$

Evidently, only the diagonal element $\langle E_{op}\rangle_{n,n}$ and four off-diagonal elements $\langle E_{op}\rangle_{n\pm1,n}$ and $\langle E_{op}\rangle_{n\pm2,n}$ have non-zero values. The matrix elements of the dipole moment are expressed as

$$\langle\mu\rangle_{m,n} = \frac{Q}{2D}\exp\left[i(m-n)\ \cot^{-1}(\xi)\right]\left[\sqrt{2(n+1)}\ \delta_{m,n+1} + \sqrt{2n}\ \delta_{m,n-1} + 2DE\ \delta_{m,n}\right].$$

$$(4\text{-}4)$$

This equation contains the diagonal element, which in fact is closely related to the parity problem of the wavefunction, as will be explained later. However, the selection rule for the dipole transition between different states

is $\Delta m = \pm 1$. Combining Eqs. (3-9) and (4-2), we arrive at the following explicit form for the dipole matrix elements:

$$\langle\mu\rangle_{n+1,n} = Q\left[\frac{(n+1)\hbar e^{\gamma t}}{2m_0\omega}\right]^{\frac{1}{2}}\left[e^{i\omega t} + \frac{\gamma}{2\omega}\sin(\omega t)\right] = \langle\mu\rangle^*_{n,n+1}$$

$$\langle\mu\rangle_{n,n} = \frac{QA(\omega',\theta)}{m_0}\cos(\omega' t - \phi_0 - \phi_1) \quad (t \neq 0) \tag{4-5}$$

$$\langle\mu\rangle_{n,n} = 0 \quad (t = 0) \quad .$$

5. Second Quantization and Transition Probability

To obtain a second-quantization formalism for a molecular system adsorbed on a solid surface, we define two functions,

$$u(t) = \frac{\xi(t) + i}{D(t)\sqrt{2[1+\xi^2(t)]}} \tag{5-1}$$

$$\eta(t) = 2i\hbar u(t)\, B_1(t) \quad ,$$

where $D(t)$ and $\xi(t)$ have already defined in Eq. (3-8) ($\eta(t)$ is not the same as the angle η in Eq. (2-14-b)). Using the relation of Eq. (3-10), we obtain

$$\eta(t)\, u^*(t) - u(t)\, \eta^*(t) = i\hbar \quad . \tag{5-2}$$

Thus we define the time-dependent annihilation and creation operators as

$$a(t) = \frac{1}{i\hbar}\left[\eta(t)(x - E(t)) - u(t)\left\{p + i\hbar[B_2 - 2B_1 E]\right\}\right]$$

$$a^{\dagger}(t) = \frac{1}{i\hbar}\left[u^{*}(t)\left\{p + i\hbar[B_2 - 2B_1 E]\right\} - \eta^{*}(t)(x - E(t))\right] \quad , \tag{5-3}$$

where $B_1(t)$, $B_2(t)$ and $E(t)$ are defined in Eq. (3-8). We note that $B_2(t) - 2B_1(t)\,E(t)$ is pure imaginary. We shall hereafter use the notation of $u(t) = u$ and $\eta(t) = \eta$. It is obvious that the non-Hermitian operators $a^{\dagger}(t)$ and $a(t)$ satisfy the commutation relation

$$[a(t),\ a^{\dagger}(t)] = 1 \quad . \tag{5-4}$$

By the definition of Eq. (5-3), we get

$$\begin{aligned} x &= u^{*}\, a(t) + u\, a^{\dagger}(t) + E \quad . \\ p &= \eta^{*}\, a(t) + \eta\, a^{\dagger}(t) - i\hbar[B_2 - 2B_1 E] \quad . \end{aligned} \tag{5-5}$$

Obviously x and p satisfy the relation $[x,p] = i\hbar$. Now we set

$$|m(t)\rangle = \frac{1}{\sqrt{m!}}\,(a^{\dagger}(t))^{m}|0(t)\rangle \tag{5-6}$$

$$a(t)|0(t)\rangle = 0 \quad . \tag{5-7}$$

Combining Eqs. (5-3) and Eq. (5-7), we obtain the time-dependent ground-state wave function

$$\psi_0(x,t) \equiv \langle x|0(t)\rangle$$

$$= \left[\frac{m_0\omega e^{\gamma t}}{\pi\hbar\zeta_1(t)}\,\frac{\xi(t)-i}{\xi(t)+i}\right]\ \exp\left[-B_1(t)x^2 + B_2(t)x - B_3(t)\right] \quad . \qquad (5\text{-}8)$$

We note that $\psi_0(x,t)$ reduces to $\psi_0(x)$ at $t = 0$, which is the ground-state wavefunction of a simple harmonic oscillator. Combining Eqs. (4-1), (5-4) and (5-5), we find the second-quantized form of the energy Hamiltonian operator, respectively, to be

$$E_{op} = \left[\frac{\eta^2}{2m_0}\,e^{-2\gamma t} + \tfrac{1}{2}m_0\omega_m^2u^2\right]a^\dagger(t)a^\dagger(t) + \left[\frac{\eta^{*2}}{2m_0}\,e^{-2\gamma t} + \tfrac{1}{2}m_0\omega_m^2u^{*2}\right]a(t)a(t)$$

$$+ \left[\frac{|\eta|^2}{m_0}\,e^{-2\gamma t} + m_0\omega_m^2|u|^2\right](a^\dagger(t)a(t)+\tfrac{1}{2}) + \left[-\frac{i\hbar\eta}{m_0}(B_2-2B_1E)e^{-2\gamma t} - uf\right.$$

$$\left. + m_0\omega_m^2uE\right]a^\dagger(t) + \left[-\frac{i\hbar\eta^*}{m_0}(B_2-2B_1E)e^{-2\gamma t} - u^*f + m_0\omega_m^2u^*E\right]a(t)$$

$$- \frac{\hbar^2}{2m_0}(B_2-2B_1E)^2e^{-2\gamma t} + \tfrac{1}{2}m_0\omega_m^2E^2 - Ef \qquad (5\text{-}9)$$

$$\hat{H} = e^{\gamma t}E_{op} \quad . \qquad (5\text{-}10)$$

Equation (5-9) yields the same energy operator expectation values listed in Eq. (4-2). It is now straightforward to obtain the second-quantized form of physical quantities such as position, momentum, dipole moment operator, etc.

Let us find the relations between the time-independent operators $a^\dagger(t)$, $a(t)$ and time-independent operators $a^\dagger, a$. The latter ones are simply defined for a simple harmonic oscillator as

$$a = \sqrt{\frac{m_0\omega_0}{2\hbar}}\left[x + \frac{ip}{m_0\omega_0}\right]$$

$$a^\dagger = \sqrt{\frac{m_0\omega_0}{2\hbar}}\left[x - \frac{ip}{m_0\omega_0}\right] \quad . \tag{5-11}$$

Substitution of the above definitions into Eq. (5-3) yields

$$\begin{aligned} a(t) &= \beta_1(t)a + \beta_2(t)a^\dagger + \beta_3(t) \\ a^\dagger(t) &= \beta_2^*(t)a + \beta_1^*(t)a^\dagger + \beta_3^*(t) \quad , \end{aligned} \tag{5-12}$$

where the coefficients are given by

$$\begin{aligned} \beta_1(t) &= \frac{\alpha_0 u(t)}{\sqrt{2}}\left[1 + \frac{2B_1(t)}{\alpha_0^2}\right] \\ \beta_2(t) &= \frac{\alpha_0 u(t)}{\sqrt{2}}\left[-1 + \frac{2B_1(t)}{\alpha_0^2}\right] \\ \beta_3 &= -u(t)B_2(t) \\ \alpha_0 &\equiv \left[\frac{m_0\omega_0}{\hbar}\right]^{1/2} \quad . \end{aligned} \tag{5-13}$$

We now find an explicit expression for the transition probability between two states $|m(t)>$ and $|n(0)>$, where $|n(0)>$ is a simple harmonic oscillator state given by

$$|n(0)> = \frac{(a^\dagger)^n}{\sqrt{n!}}\,|0(0)> \quad . \tag{5-14}$$

Here $|0(0)\rangle$ is the well-known ground state of the simple harmonic oscillator. Using Eqs. (5-6), (5-12) and (5-14), we get

$$\langle m(t)|n(0)\rangle = \frac{1}{\sqrt{m!n!}} \langle 0(t)|(a(t)^m(a^\dagger)^n|0(0)\rangle$$

$$= \frac{1}{\sqrt{m!n!}} \langle 0(t)|[\beta_1 a + \beta_2 a^\dagger + \beta_3]^m(a^+)^n|0(0)\rangle \quad , \qquad (5\text{-}15)$$

where $|0(t)\rangle$ is the time-dependent ground state of the damped driven harmonic oscillator, given by Eq. (5-8). $\langle m(t)|n(0)\rangle$ represents the probability amplitude of finding the system in a state $|m(t)\rangle$ at time t, given that the system was in a state $|n(0)\rangle$ at time zero. To calculate the right side of Eq. (5-15), we need to rearrange the operators in normal order, which means that all the $a^\dagger$'s appear to the left of the a's. The normal-ordered arrangement is carried out by introducing a normal-ordering operator[23] N such that

$$[\beta_1 a + \beta_2 a^\dagger + \beta_3]^m(a^\dagger)^m = N\left[\left\{\alpha^* + \frac{\partial}{\partial\alpha}\right\}^n\left\{\beta_1\alpha + \beta_2\alpha^* + \beta_3\right\}^m\right] \quad , \qquad (5\text{-}16)$$

where α and α^* are complex c-numbers. With this method, we obtain

$$[\beta_1 a + \beta_2 a^\dagger + \beta_3]^m(a^\dagger)^n$$

$$= \sum_{k_1=0}^{m} \sum_{k_2=0}^{m-k_1} \sum_{k_3=0}^{n} \binom{m}{k_1}\binom{m-k_1}{k_2}\binom{n}{k_3} \frac{k_1!}{(k_1-k_3)!}$$

$$\times (a^\dagger)^{n+k_2-k_3}(a)^{k_1-k_3} \beta_1^{k_1} \beta_2^{k_2} \beta_3^{m-k_1-k_2} \quad . \qquad (5\text{-}17)$$

Evidently $a^{k_1-k_3}|0(0)\rangle$ vanishes for all k_3's except that $k_3 = k_1$. We have used above the notation $\beta_1 = \beta_1(t)$, $\beta_2 = \beta_2(t)$ and $\beta_3 = \beta_3(t)$, which will be used hereafter. $\left\{\ \right\}$ means binomial distribution.

Substitution of Eq. (5-17) into Eq. (5-15) gives

$$\langle m(t)|n(0)\rangle = \frac{1}{\sqrt{m!n!}} \sum_{k_1}^{[m,n]} \sum_{k_2}^{m-k_1} \binom{m}{k_1}\binom{m-k_1}{k_2}\binom{n}{k_1} \beta_1^{k_1} \beta_2^{k_2} \beta_3^{m-k_1-k_2} \times \langle 0(t)|(a^+)^{n-k_1+k_2}|0(0)\rangle \quad , \tag{5-18}$$

where $[m,n] = \min(m,n)$ implies the smaller of the two. Using Eqs. (5-8) and (5-14), we find

$$\langle 0(t)|(a^+)^{n-k_1+k_2}|0(0)\rangle = \left[\frac{\alpha_0}{\sqrt{\pi}\ 2^{n-k_1+k_2}}\right]^{1/2} \left[\frac{m_0\omega\ e^{\gamma t}}{\pi\hbar\zeta_1}\frac{\xi+i}{\xi-i}\right]^{1/4} \exp[-B_3^*] \times \int_{-\infty}^{\infty} dx\ \exp\left[-\left\{B_1^* + \frac{\alpha_0^2}{2}\right\}x^2 + B_2^* x\right] H_{n-k_1+k_2}(\alpha_0 x) \quad . \tag{5-19}$$

To integrate the right side of Eq. (5-19), we introduce a generating function for the Hermite polynomial He(y) such that

$$He(y) = \left[\frac{\partial^\ell}{\partial s^\ell}\exp\left\{-s^2 + 2sy\right\}\right]_{s=0} \quad . \tag{5-20}$$

Then we have

$$I \equiv \int_{-\infty}^{\infty} dx \exp\left[-\left\{B_1^* + \frac{\alpha_0^2}{2}\right\}x^2 + B_2^* x\right] H_{n-k_1+k_2}(\alpha_0 x)$$

$$= \left[\frac{d^{\ell}}{ds^{\ell}} I(s)\right]_{s=0} \qquad (\ell = n-k_1+k_2) \tag{5-21}$$

where

$$I(s) = \frac{e^{-s^2}}{\alpha_0} \int_{-\infty}^{\infty} dy \exp\left[-\frac{\alpha_0^2 + 2B_1^*}{2\alpha_0^2} y^2 + \frac{2\alpha_0 s + B_2^*}{\alpha_0} y\right] , \tag{5-22}$$

which is easily integrated. Substituting the result of integration into Eq. (5-21) and performing some calculations, we obtain the following result:

$$I = \left[\frac{2\pi}{\alpha_0^2 + 2B_1^*}\right]^{1/2} \exp\left[\frac{(B_2^*)^2}{2(\alpha_0^2 + 2B_1^*)}\right] \sum_{k_3=0}^{n-k_1+k_2} \binom{n-k_1+k_2}{k_3} \frac{k_3!}{(k_3/2)!} \left[\frac{2B_1^* - \alpha_0^2}{2B_1^* + \alpha_0^2}\right]^{k_3/2}$$

$$\times \left[\frac{2\alpha_0 B_2^*}{\alpha_0^2 + 2B_1^*}\right]^{n-k_1+k_2-k_3} \qquad (k_3: \text{ even}) \tag{5-23}$$

By Eqs. (5-18), (5-19) and (5-23), we obtain the probability amplitude as

$$\langle m(t)|n(0)\rangle = \frac{1}{\sqrt{2^n m!n!}} \left[\frac{2\alpha_0}{\alpha_0^2 + 2B_1^*}\right]^{1/2} \left[\frac{m_0\omega\, e^{\gamma t}}{\hbar\zeta_1} \frac{\xi + i}{\xi - i}\right]^{1/4} \exp\left[-B_3^*(t) + \frac{(B_2^*)^2}{2(\alpha_0^2+2B_1^*)}\right]$$

$$\times \sum_{k_1=0}^{[m,n]} \sum_{k_2=0}^{m-k_1} \sum_{k_3=0}^{n-k_1+k_2} \binom{m}{k_1}\binom{m-k_1}{k_2}\binom{n}{k_1}\binom{n-k_1+k_2}{k_3} \frac{(k_3)!}{(k_3/2)!} \frac{\beta_1^{k_1}\,\beta_2^{k_2}\,\beta_3^{m-k_1-k_2}}{2^{(k_2-k_1)/2}}$$

$$\times \left[\frac{2B_1^* - \alpha_0^2}{2B_1^* + \alpha_0^2}\right]^{k_3/2} \left[\frac{2\alpha_0 B_2^*}{2B_1^* + \alpha_0^2}\right]^{n-k_1+k_2-k_3} \qquad (k_3: \text{ even}) \quad . \qquad (5\text{-}24)$$

The transition probability between the DDHO state $|m(t)>$ and the simple harmonic oscillator state $|n(0)>$ is given by

$$P_{m,n}(t) = |<m(t)|n(0)>|^2 \quad . \qquad (5\text{-}25)$$

6. Results and Discussion

We have modeled a molecule adsorbed on a dielectric solid surface as a damped harmonic oscillator driven by a time-dependent electric field, consisting of a primary and a secondary field. The Hamiltonian of this modeled system is not identical to the mechanical energy operator, showing a general characteristic of the Kalidola-Kanai-type Hamiltonian. The propagator of Eq. (3-4) has the same structure as that of Gerry[24] when there exists no driving force, and is similar to that of Dodonov et al.[4] The wavefunction of Eq. (3-7) has no definite parity, which can be easily seen from the matrix elements of x and x^2,

$$<m(t)|x|n(t)> = \sqrt{n+1}\; u(t)\; \delta_{m,n+1} + \sqrt{n}\; u^*(t)\; \delta_{m,n-1} + E(t)\delta_{m,n} \quad . \qquad (6\text{-}1)$$

$$<m(t)|x^2|n(t)> = \sqrt{(n+1)(n+2)}\; u^2(t)\; \delta_{m,n+2} + \sqrt{n(n-1)}\; u^{*2}(t)\delta_{m,n-2}$$

$$+ \left[(2n+1)|u(t)|^2 + E^2(t)\right] \delta_{m,n}$$

$$+ 2\sqrt{(n+1)}\, u(t)E(t)\, \delta_{m,n+1} + 2\sqrt{n}\, u^*(t)E(t)\, \delta_{m,n-1} \quad . \quad (6\text{-}2)$$

If $\psi_m(x,t)$ and $\psi_n(x,t)$ have definite parity and both have the same (even or odd) parity, $\langle m(t)|x|n(t)\rangle$ must be always zero, while if they have opposite parities, $\langle m(t)|x^2|n(t)\rangle$ must vanish. Equations (6-1) and (6-2), however, do not satisfy this rule. This property of the wavefunctions does not result from the decay characteristic of the system, but from the interaction between the system and the driving force, because the wavefunction of a damped (not driven) harmonic oscillator has a definite parity.[21] Due to the absence of definite parity of the wavefunction, the diagonal element of the dipole moment takes the form given in Eq. (4-5), in contrast to a simple harmonic oscillator. The real part of the off-diagonal elements of the dipole moment is the same as that of the classical case.[25]

Because of the time-dependence $|\psi_n(x,t)|^2$, the expectation values of E_{op} (or $\hat{H}$) and other physical quantities do not stay constant in time. The diagonal parts of E_{op} and $\hat{H}$ are approximated as,

$$\langle E_{op}\rangle_{n,n} \simeq (n + \tfrac{1}{2})\hbar\omega\, e^{-\gamma t} + \frac{g^2(\omega,'\theta)}{2m_0[\omega_m^2 - \omega'^2 + \gamma\omega']} \quad (6\text{-}3)$$

$$\langle \hat{H}\rangle_{n,n} = e^{\gamma t} \langle E_{op}\rangle_{n,n} \quad . \quad (6\text{-}4)$$

The first term in Eq. (6-3) shows the decay of the quantum state, and the second term represents the energy absorption from the external field; these processes are related to the lineshape in optical phenomena. When there

exists no driving force ($g(\omega',\theta) = 0$), Eqs. (6-3) and (6-4) reduce to those of a damped harmonic oscillator.[26] Hence, we can say that for a damped harmonic oscillator the expectation values of $\hat{H}$ stays constant in time and those of E_{op} do not, while for a damped driven oscillator the expectation of both operators vary in time. Of course, for the simple harmonic case, the two operators are identical and their expectation values remain stationary.

The method adopted in Sec. 5 to calculate $P_{m,n}(t)$ is different from that of others,[20,27] and Eq. (5-24) is of a new form. In practice, however, it is a formbidable task to get the transition probability, $P_{m,n}$, from Eq. (5-24). Even for the simplest two-level case such that $|m(t)> = |1(t)>$ and $|n(0)> = |0(0)>$, the calculation is quite tedious. Hence, we simply write the result for this case:

$$P_{1,0} = |<1(t)|0(0)>|^2$$

$$= 2\alpha_0^2 E^2(t)\, e^{\gamma t/2}\left[1 - e^{\gamma t} + 2e^{-2\gamma t} + (1+ e^{\gamma t})\, \zeta_3^2(t)\right]\left[1 + e^{-\gamma t}\right]^{-3}$$

$$\times \exp\left[- \frac{\alpha_0^2 E(t)^2 \left\{1 + e^{\gamma t}\zeta_3^2(t)\right\}}{1 + e^{-\gamma t}}\right] , \qquad (6\text{-}5)$$

where we have used the approximation $D \simeq \alpha_0 \exp(\gamma t/2)$, since in a real system $\omega \simeq \omega_0$ and $\gamma << \omega$.

Here we note that the transitions should occur on a time scale shorter than the system damping time[23] γ^{-1}, i.e., $\gamma t << 1$. Thus Eq. (6-5) can be approximated as

$$P_{1,0}(t) = I(\omega',t) \exp[-I(\omega',t)] \qquad (6\text{-}6)$$

$$I(\omega',t) = \frac{\alpha_0^2 g^2(\omega',\theta)\left[\cos^2(\omega' t-\phi_0-\phi_1) + (\frac{\omega'}{\omega})^2 \sin^2(\omega' t-\phi_0-\phi_1)\right]}{2m_0^2\left[\left\{\omega^2 - \omega'^2 + \gamma^2/4\right\}^2 + (\gamma\omega')^2\right]} \quad . \quad (6\text{-}7)$$

The transition probability depends strongly on the external driving force and the energy transfer mechanism. Around the resonance frequencies $\omega' \simeq \omega^2 + \gamma^2/4 = \omega_m^2$, Eq. (6-9) becomes

$$I_R(\omega') = \frac{\alpha_0^2 g^2(\omega',\theta)}{2m_0^2}\left[\left\{\omega^2 - \omega'^2 + \gamma^2/4\right\}^2 + (\gamma\omega')^2\right]^{-1} \quad , \quad (6\text{-}8)$$

where this form is related to the lineshape in optical phenomena. Application of the results in this work to optical phenomena on a dielectric surface, to finding the coherent states[28] and to the time-dependent invariant[29] problem will be left for further study.

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